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STATISTICAL EXPLANATION OF SPONTANEOUS FREEZING OF WATER DROPLETS

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SUMMARY

A statistical theory based on the presence of small crystallization nuclei suspended in water is developed to explain experimental results showing that on the average small droplets can be supercooled to lower temperatures than large ones. Small nuclei of crystallization are assumed responsible for causing supercooled water to freeze spontaneously.

The average behavior of supercooled droplets is reproduced on the basis of probability theory with an assumed distribution of crystallization nuclei with respect to the temperatures at which the nuclei cause freezing. The most probable distribution curves of spontaneous freezing temperatures for water droplets of various sizes within the size range found in clouds are obtained.

INTRODUCTION

The prolonged operation of unprotected aircraft in supercooled clouds has been found to be a hazard. For the icing hazard to be overcome, the physical conditions under which supercooled clouds exist must be understood. The physics of supercooling and freezing is incompletely understood, as shown by conflicting opinions expressed in the literature. The following factors have been described as causes of freezing in supercooled water samples: (1) introduction of ice crystal; (2) mechanical shock, such as vibration, scratching of solid surfaces together in water sample, and sound waves; (3) length of time water has existed in supercooled state; (4) impurities; and (5) droplet size.

Investigators seem to agree that an ice crystal introduced into a sample of supercooled water will cause the water to freeze. Recent experiments by Dorsey (reference 1) indicate that mechanical shock, however, is of little importance in freezing of supercooled water; likewise, time apparently is not a factor. From the extensive investigation of reference 1, it is concluded that small solid particles suspended in

the water or irregularities on the container surface cause the supercooled water to freeze at a given temperature. These hypothetical particles are called motes and the temperature at which a sample freezes without any apparent external stimuli is called the spontaneous freezing temperature. The spontaneous freezing temperature was found in most cases to be a characteristic of each sample, which led to the mote hypothesis.

The observations described in reference 1 have been substantiated somewhat in reference 2 in which a statistical investigation of water-droplet size as a factor in determining the spontaneous freezing temperatures of the droplets is presented. By observation of a large number of droplets, the following results were obtained: (1) The frequency-distribution curve with respect to spontaneous freezing temperature of a given droplet size was found to have a marked peak or mode; and (2) the average spontaneous freezing temperature of each size group decreased with decreasing droplet size.

In reference 3, the conclusions are made from observation of a number of droplets that the spontaneous freezing temperature of droplets from 400 microns down to approximately 50 microns rapidly decreased with size and that droplets larger than 400 microns had a practically constant freezing temperature. The results of reference 3 are qualitatively verified in reference 2 but only to the extent that the average freezing temperature for a given size was found to be a function of the size.

Similar results of a qualitative nature have been obtained with substances other than water. In reference 4, the possible degree of supercooling in sulphur droplets was found to increase with decreasing droplet diameter. In addition, it was found more difficult to supercool sulphur droplets on a metal surface, such as brass or aluminum, than on a glass surface. The effect of droplet size on spontaneous freezing temperature was ascribed to the fact that smaller droplets are less susceptible to external influences than larger droplets. The surface was thought to have an influence on the crystallizing forces within the supercooled droplet. Substances such as gold, platinum, rhodium, mercury, and other metals have been supercooled to a greater extent in the form of small particles than in bulk (reference 5). The effect of droplet size on spontaneous freezing temperature is ascribed in reference 5 to the presence of small particles of impurity in the liquid. When the liquid is broken up into small droplets the foreign particles are isolated in a few drops allowing the remainder to supercool to the temperature at which molecules of the liquid combine to form crystals without the aid of motes.

The hypothesis of reference 5 combined with the mote concept of reference 1 indicates a way of explaining the statistical results presented in reference 2. A statistical theory that accounts for the two conclusions of reference 2 on the basis of motes or any other agent causing nuclei of crystal growth to form was developed at the NACA Lewis laboratory and is presented herein.

THEORY

An assumption is made that a large number of motes are present in liquid water. Also, each mote is assumed to be associated with a definite spontaneous freezing temperature. The freezing temperature of a water sample is governed by the mote in the sample that is associated with the highest freezing temperature.

In the experiment reported in reference 2, water was condensed from the atmosphere in the form of frost on a polished metal surface by lowering its temperature to approximately -35° C. The frost was subsequently melted and droplets formed on the surface. Repeated application of this procedure made a large number of droplets of various sizes available for determining spontaneous freezing temperatures. Because the water condensed from the atmosphere was a very small fraction of the total amount of water available in the form of vapor, the process was practically the same as drawing small samples of volume ΔV from a large reservoir of liquid water of volume V. Because motes of all kinds are assumed to be present everywhere, it is reasonable to consider them to be present in the same relative proportions in the hypothetical volume of liquid water V.

The problem to be solved is the determination of the most probable frequency-distribution curve of spontaneous freezing temperatures subject to the following conditions:

(1) There are $N_0, N_1, N_2, N_3, \ldots N_T, \ldots$ motes of kinds $0, 1, 2, 3, \ldots T, \ldots$, respectively, present in the volume V, where T is the absolute value of the temperature in °C at which the mote of kind T causes water to freeze.

(2) The small volumes that are drawn from V are of volume ΔV, and the total number of volumes ΔV obtainable from V is $V/\Delta V = \mu$.

(3) The number of draws in each set of draws from V is so small that μ is practically unchanged while a set is being drawn.

First the motes of kind T are considered. There are N_T motes available for distribution among the μ small volumes ΔV, into which V may be divided. The total number of ways of distributing N_T objects among μ cells is μ^{N_T}. Each way of distributing N_T objects may be called a complexion. Next, regarding the group of all possible complexions, there are μ cells in each complexion and therefore μ^{N_T+1} cells in all the complexions. The probability of drawing a small volume in one draw with no motes of kind T in it is $\frac{Q}{\mu^{N_T+1}}$, where Q is the number of cells that among the μ^{N_T+1} cells in all the possible complexions contain no motes. The probability of drawing a small volume containing one or more motes is $1 - \frac{Q}{\mu^{N_T+1}}$.

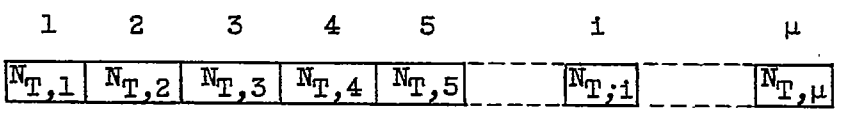
A simple example should serve to make the foregoing logic clearer. Two motes are supposed to exist in a volume of water V. From V a volume $\Delta V = \frac{1}{2} V$ is to be drawn. The probabilities that in a single draw one or more motes will be in the half volume drawn or that no motes will be contained in it are to be determined. For solution of the problem, the volume V may be schematically represented by two squares of equal area side by side. Thus, if the motes are numbered 1 and 2 for identification, the complexions may be pictured as follows:

1 | 2	2 | 1	1,2 |	| 1,2

The number of possible complexions is $\mu^{N_T} = 2^2 = 4$ and the total number of volumes or cells in all the complexions is $\mu^{N_T+1} = 2^3 = 8$. The number of cells containing no motes is two and the number containing one or more motes is six. The probability of drawing a cell with no motes in it is therefore $\frac{Q}{\mu^{N_T+1}} = \frac{1}{4}$ and with one or more motes in it, $1 - \frac{Q}{\mu^{N_T+1}} = \frac{3}{4}$.

In the preceding example a particular case has been evaluated. General expressions for the probabilities must now be obtained in terms of μ and N_T. As in the previous example, cells are lined up side by side numbered from 1 to μ. In a given complexion there are $N_{T,1}$, $N_{T,2}$, . . . $N_{T,\mu}$ motes in the cells 1, 2, . . . μ, respectively, where

the second subscript is the cell number and $N_{T,i}$ is the number of motes in the i^{th} cell:



The total number of motes causing freezing at a temperature of $-T^{\circ}$ C is

$$N_T = N_{T,1} + N_{T,2} + \cdots + N_{T,\mu}$$

The total number of complexions having $N_{T,1}$ equal to 0 is $(\mu-1)^{N_T}$, because N_T objects are restricted to distribution among $\mu-1$ cells by the condition $N_{T,1}=0$. Likewise, there are $(\mu-1)^{N_T}$ complexions subject to each of the conditions $N_{T,2}=0, \ldots N_{T,i}=0, \ldots N_{T,\mu}=0$, respectively. Thus, there are altogether $\mu(\mu-1)^{N_T}$ cells among the μ^{N_T} complexions that contain no motes. But there is a total of μ^{N_T+1} cells in all the possible complexions. The probability of drawing a cell with no motes in it is therefore $\left(\frac{\mu-1}{\mu}\right)^{N_T}$ and the probability of drawing one with one or more motes in it is $1 - \left(\frac{\mu-1}{\mu}\right)^{N_T}$.

In order to complete the solution of the problem with all kinds of mote present, the probability $P(T,\mu)$ of drawing a cell with one or more motes causing freezing at a given temperature and none causing freezing at a higher temperature must be found. The probability of drawing a cell that would freeze at a temperature of $-T^{\circ}$ C is equal to the product of the probability of drawing a cell with no particles of kinds 0, 1, . . . T-1 and the probability of drawing a cell with one or more particles of kind T, that is,

$$P(T,\mu) = \left(\frac{\mu-1}{\mu}\right)^{N_0+N_1+N_2+\cdots+N_{T-1}} \left[1 - \left(\frac{\mu-1}{\mu}\right)^{N_T}\right] \qquad (1)$$

The most probable frequency-distribution curve of spontaneous freezing temperature for a given value of μ is given by equation (1).

Because the quantity $\mu = V/\Delta V$ contains both ΔV and V, the question arises as to the possible dependence of $P(T,\mu)$ on V as well as ΔV. It can be shown that for $\Delta V/V$ small enough so that terms of the second or higher order may be neglected, the function $P(T,\mu)$ is independent of V. Samples of volume ΔV are drawn from two large volumes V and V' such that $\Delta V/V$ and $\Delta V/V'$ are very small. The mote densities (numbers per unit volume) of various kinds are the same in both volumes, namely $\rho_0, \rho_1, \rho_2, \ldots \rho_T$. The corresponding expressions for $P(T,\mu)$ are

$$P = \left(1 - \frac{\Delta V}{V}\right)^{(\rho_0+\rho_1+\rho_2+ \ldots + \rho_{T-1})V} \left[1 - \left(1 - \frac{\Delta V}{V}\right)^{\rho_T V}\right],$$

and

$$P' = \left(1 - \frac{\Delta V}{V'}\right)^{(\rho_0+\rho_1+\rho_2+ \ldots + \rho_{T-1})V'} \left[1 - \left(1 - \frac{\Delta V}{V'}\right)^{\rho_T V'}\right]$$

With only the first two terms in the binominal expansion of $\left(1 - \frac{\Delta V}{V}\right)^{(\rho_0+\rho_1+\rho_2+ \ldots + \rho_T)V}$ and $\left(1 - \frac{\Delta V}{V}\right)^{\rho_T V}$, it is found that

$$P = P'$$

which proves $P(T,\mu)$ to be independent of the choice of V provided $\Delta V/V$ is small enough. Even the higher-order terms are practically independent of V if the exponents are large compared to 1. (See the appendix.)

With the expression for $P(T,\mu)$ formulated in equation (1), a mote-density function of freezing temperature must be found such that the resulting probability function agrees at least in its general characteristics with the distribution curves presented in reference 2. The $(T+1)^{th}$ term of the geometric progression

$$a, ar, ar^2, \ldots ar^T, \ldots$$

where a is the number of motes in the volume V causing freezing at 0° C and r is an arbitrary constant, was found to be a suitable mote frequency-distribution function. Thus the sum of all motes causing freezing between 0° C and $-T^\circ$ C in V is

$$\sum_{0}^{T} N_T = \sum_{0}^{T} ar^T = a\left(\frac{r^{T+1}-1}{r-1}\right)$$

The following form of equation (1) is obtained by substitution of the foregoing expression:

$$P(T,\mu) = \left(\frac{\mu-1}{\mu}\right)^{a\left(\frac{r^T-1}{r-1}\right)} \left[1 - \left(\frac{\mu-1}{\mu}\right)^{ar^T}\right] \tag{2}$$

because

$$N_0+N_1+N_2+N_3+ \cdots +N_{T-1} = a\left(\frac{r^T-1}{r-1}\right)$$

The nature of equation (2) is evident in figure 1 where curves corresponding to particular values of μ and ρ_0 and various values of r are plotted. The probability curves all have a maximum and are somewhat unsymmetrical. Furthermore, as r increases the maximum value of P increases and the peak of the curve becomes narrower. The curves of figure 1 are comparable in form to the frequency-distribution curves of reference 2.

In order to fit the experimental average freezing temperature-droplet size curve with the theoretical curve, the mode (or maximum) of $P(T,\mu)$ is found by taking the derivative $dP(T,\mu)/dT$ and solving the equation

$$\frac{dP(T,\mu)}{dT} = 0$$

for T. The mode or the maximum of the probability curve, which is almost symmetrical, is close enough to the average so that they may be considered equal (table I).

By performing the foregoing operations, the following equation for the mode T_M as a function of μ, a, and r is obtained:

$$T_M = \frac{\log(\log r) - \log\left(\log\frac{\mu}{\mu-1}\right) - \log a}{\log r} \tag{3}$$

Equation (3) is now reduced to a simple approximate form. Because V is much larger than ΔV, second- or higher-order terms in $\Delta V/V$ are neglected with the result that

$$\frac{\mu}{\mu-1} = \frac{1}{1 - \frac{\Delta V}{V}} \cong 1 + \frac{\Delta V}{V} \tag{4}$$

and

$$\log \frac{\mu}{\mu-1} \cong \log \left(1 + \frac{\Delta V}{V}\right) \cong 0.4343 \frac{\Delta V}{V} \tag{5}$$

In the experimental curve of reference 2, T_M is plotted as a function of the diameter D of a hemispherical drop of volume ΔV so that for comparison of theory with experiment equation (4) becomes

$$\frac{\mu}{\mu-1} = \frac{1}{1 - \frac{\pi D^3}{12V}}$$

or

$$\log \frac{\mu}{\mu-1} \cong 0.4343 \frac{\pi D^3}{12V} \tag{6}$$

Furthermore, the mote-density function is $\rho_T = \frac{a}{V} r^T$, and the mote-density constant is $\rho_0 = \frac{a}{V}$. Thus, by substitution of equation (6) in equation (3)

$$T_M = \frac{\log (\log r) - 3 \log D + \log \frac{8.78}{\rho_0}}{\log r} \tag{7}$$

is obtained. As a result of the assumed mote-density function, T_M is therefore to the first order of approximation a linear function of log D. The linear relation between T_M and log D is a basic one that can readily be compared with the experimental data of reference 2.

The slope of the linear equation (7) is

$$\frac{T_{2,M}-T_{1,M}}{\log D_2 - \log D_1} = -\frac{3}{\log r} \tag{8}$$

where the subscripts 1 and 2 indicate two distinct values of T_M corresponding to two droplet sizes D_1 and D_2, respectively. The constant ρ_0 is found from equation (7), after setting $T_M = 0$, to be

$$\rho_0 = \frac{8.78 \log r}{D_0^3} \tag{9}$$

where D_0 is the value of D when $T_M = 0$. From equation (8), the slope of equation (7) is apparently a function of r alone, and ρ_0 according to equation (9) determines the intercept. Equations (8) and (9) will be subsequently useful in evaluating the constants r and ρ_0 from the slope and the intercept of the experimental average temperature-log D curve. Then with the constants ρ_0 and r known, the theoretical probability curves may be computed from equation (2) and compared with the experimental frequency-distribution curves of reference 2.

In addition to equations (8) and (9) defining the mode and the intercept, an approximate transformation equation is derived in the appendix. With this transformation, a probability curve for one set of values of the parameters ρ_0 and ΔV can be transformed simply to a curve corresponding to another set of values. If r is kept constant and it is desired to transform from a distribution curve for a volume ΔV_1 and mote-density constant $\rho_{0,1}$ to another for ΔV_2 and $\rho_{0,2}$, then for a given value of the probability P the value of the freezing temperature T_2 corresponding to ΔV_2 and $\rho_{0,2}$ is related to T_1 corresponding to ΔV_1 and $\rho_{0,1}$ by

$$T_2 = T_1 + \frac{\log\left(\rho_{0,1}\Delta V_1 / \rho_{0,2}\Delta V_2\right)}{\log r} \tag{10}$$

This transformation is possible, because the family of curves corresponding to all values of ΔV and ρ_0 are identical in size and shape but are displaced in the T coordinate. (See the appendix.)

A method of transformation from a curve for r_1 to another for r_2, keeping ρ_0 and ΔV constant, is unavailable, but a set of curves for various values of r is given in figure 1 from which curves for other values of ΔV and ρ_0 may be computed using the preceding transformations.

RESULTS AND DISCUSSION

For comparison of the theory of this report with the experimental results of reference 2, the data of reference 2 for the average freezing temperature-size curve are replotted on semilog paper, and an irregular curve that can be fitted reasonably well with a straight line is obtained (fig. 2). This result agrees with the linear relation between T_M and log D indicated by equation (7). The slope of the straight line, as drawn in figure 2, is -7.21 and the value of D_0 is 24 (cm). From the slope, the value r is found by equation (8) to be 2.60 and, from the intercept D_0 and equation (9), ρ_0 has the value 2.64×10^{-4} (cm^{-3}). The linear equation that best fits the data of reference 2 is therefore

$$T_M = 9.95 - 7.21 \log D$$

With the constants r and ρ_0 now known, it is possible to compute the probability curves for various droplet sizes. A comparison between these curves and the corresponding experimental frequency-distribution curves of reference 2 is given in figure 3 where histograms of the experimental data are reduced to the probability scale. Figures 3(b) to 3(d) represent the results obtained for the droplet sizes with the greatest amount of experimental data, and figures 3(a) and 3(e) represent the results for the extremes of the size range investigated where the data were limited. In the computation of the probability curves of figure 3, a convenient value of $V = 10^5$ (cm^3) was assumed. The value of V does not influence the curves if it is large compared with ΔV.

The agreement between the theoretical and experimental curves in figure 3 is qualitatively very good, but the following differences in detail exist. The modes of the theoretical curves differ from those of the experimental curves corresponding to the deviation of experimental points from the straight line drawn through them in figure 2. The experimental probability curves are broader and have less pronounced peaks than the theoretical curves. The standard deviations (root mean squares of the deviations from the mean freezing temperature) of the theoretical curves are constant and equal to 1.38° C, but the standard

deviations of the experimental curves are between 2 and 4 times as great and are roughly constant in the size range below 100 microns (fig. 4). Above 100 microns there is a sharp increase in the standard deviation of the experimental data to a higher approximately constant value of 3.8.

The foregoing difference between the experimental and theoretical curves cannot be ascribed to the fact that the experimental data are grouped into narrow droplet-size ranges to provide the freezing-temperature distribution curves for a given average droplet size. A composite theoretical curve formed by combining theoretical curves from the middle and the two extremes of the experimental-size group differed very little from the unmodified theoretical curve, as shown in figure 3(c).

Better agreement between theory and experiment is obtained if several different mote-density functions are postulated and the corresponding theoretical curves combined. This procedure may be justified, because the experimental data were taken on several days distributed over a period of three months. Data taken each day covered almost the entire range of droplet sizes investigated. If impurities were the active agent, the mote-density function could change from day to day during that time. Thus, the combination of data taken at different times could easily broaden the experimental distribution curves as compared to the theoretical curves. Changes in r and ρ_0 could modify the slope and the intercept, respectively, of the T_M - log D curve (fig. 2).

The modes of the theoretical distribution curves may be shifted without changing the slope of the T_M-log D curve by varying the constant ρ_0. The weighted combination of several curves corresponding to values of ρ_0 between 10^{-5} and 10^{-3} (cm^{-3}) (see table II) results in theoretical curves that fit the experimental curves much better than the unmodified theory, as shown in figure 3. The modified theoretical curves, however, have a constant standard deviation equal to 2.12° C, which still does not agree with the standard deviations of the experimental curves, as shown in figure 4. Better agreement might have been obtained by varying the values of r as well as of ρ_0; but the additional work involved in varying r was not considered worthwhile, because the variation of ρ_0 was only postulated to demonstrate the plausibility of the hypothesis concerning the behavior of the experimental standard deviations. The good agreement obtained between theory and experiment indicates that variation of the mote-density function among several groups of combined data can account for the discrepancy between theory and experiment.

Deviations from the most probable curves may by chance occur in the observed distribution curves, but deviations of a given magnitude become less probable as the number of observations increases. This principle is illustrated by the greater regularity of distribution curves based on a large number of observed droplets as compared with those based on a small number of droplets. For example, the curves in figures 3(a) and 3(e) for which 39 and 35 droplets, respectively, were observed are quite irregular as compared with the curve in figure 3(c), for which 692 droplets were observed.

CONCLUDING REMARKS

In the derivation of the foregoing statistical theory, emphasis has been placed on the mote hypothesis of Dorsey, but the theory is also applicable to homogeneous nucleation as described by Volmer (reference 6). According to reference 6, the random small-scale fluctuations in an impurity-free supercooled liquid may cause crystal nuclei to form, resulting in crystal growth from the mother liquid. The presence of motes in the liquid would mask the homogeneous nucleation. If it were possible to remove all foreign nuclei, then the mote distribution function N_T would merely be renamed the homogeneous nucleus distribution function and the logic of the theory in this report would apply as in the case of the motes except that N_T would now be a function increasing with time. Thus, a container of liquid kept at a constant temperature of supercooling should freeze after a period of time. But the experience that Dorsey (reference 1) had in maintaining three test tubes at a temperature between -8.0° and -10.3° C for 312 days might seem to invalidate the homogeneous-nucleation theory. The apparent inconsistency that exists between the results of reference 1 and those expected from the homogeneous-nucleation theory may possibly be resolved by the following logic. The temperature range in which the experiment of reference 1 was performed may be one of low nucleus-formation probability even over a period of 312 days. But if the probability of nucleus formation increases very rapidly at some temperature much lower than -10° C, the most probable length of time that a given water sample can remain at a low constant temperature of supercooling may be sufficiently reduced to make maintenance of the water sample in the supercooled state for a very long time practically impossible.

If the spontaneous freezing temperatures of droplets are principally determined by the presence of motes, the results of this report can be extended to supercooled clouds, because there should be no essential difference between the droplets supported on a surface and the droplets suspended in the atmosphere except for possible variations in the mote distribution curves as a function of time and place. The

results of this report indicate that no well-defined temperature exists at which supercooled cloud droplets are transformed into ice particles. As the temperature is decreased in a given cloud, more and more droplets will tend to freeze until a point is reached at which very few droplets are left unfrozen. For example, in a cloud of uniform droplet size with hemispherical diameter D of 34.5 microns or an actual spherical droplet diameter of 27.4 microns which is fairly common in clouds, practically all the droplets would be frozen at a temperature of -34° C. On the other hand, practically all the droplets in the cloud would remain unfrozen down to a temperature of -18° C and only about half would be frozen at a temperature of -28° C. In clouds with a droplet size of 5 microns or greater, therefore, very few supercooled droplets exist at temperatures lower than -35° C and the existence of an icing cloud at such low temperatures is probably an unusual occurrence.

The relative proportions of frozen and supercooled droplets in a cloud are important in determining the stability of the cloud. A cloud is considered to be stable if factors causing rapid dissipation of the cloud are absent. One of the factors that may cause a supercooled cloud to become unstable is the existence of ice particles in the cloud. Ice particles in a supercooled cloud have a lower vapor pressure than the surrounding supercooled drops. As a result of the vapor-pressure gradient existing between the liquid droplets and ice particles, water tends to evaporate from the droplets and condense on the ice particles. Thus, if ice particles are present in sufficient number distributed evenly throughout the cloud, the ice particles will grow at the expense of the supercooled drops until they fall out of the cloud in the form of precipitation (reference 7). If too few ice particles appear in a supercooled cloud, they will grow and fall out of the cloud leaving it practically intact. On the other hand, if too many ice particles appear, the cloud is merely transformed to an ice-particle cloud. The presence of ice crystals in supercooled clouds is considered to be the principal factor initiating precipitation.

Determination of whether the statistics of freezing are affected by change of environment requires further investigation. For example, if impurities are the cause of freezing in supercooled water, then the average freezing temperature of a given droplet size should be depressed by maintaining as high a degree of cleanliness as possible. In addition, if cleanliness is found to have the anticipated influence, the effect of adding finely divided materials of known constitution to water can be investigated. In the experiments on supercooled water that have been

conducted up to the present time, the water has always been in contact with a container or support. In order to attain conditions that approach those in clouds, a method of investigating the freezing-temperature statistics of unsupported droplets must be found.

1419

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
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APPENDIX - DERIVATION OF TRANSFORMATION EQUATIONS

Equation (10) for transformation of a probability curve corresponding to one set of values of the parameters ΔV and ρ_0 to another set of values is derived from equation (2) written in the form

$$P(T,\Delta V,\rho_0,r) = \left(1 - \frac{\Delta V}{V}\right)^{\rho_0\left(\frac{r^T-1}{r-1}\right)V} \left[1 - \left(1 - \frac{\Delta V}{V}\right)^{\rho_0 r^T V}\right] \tag{12}$$

Equation (12) must first be expanded in a series to obtain an approximate expression, which is used to show the dependence of P on ΔV and ρ_0. The members of equation (12), $\left(1 - \frac{\Delta V}{V}\right)^{\rho_0\left(\frac{r^T-1}{r-1}\right)V}$ and $\left(1 - \frac{\Delta V}{V}\right)^{\rho_0 r^T V}$, are written in a binomial expansion as follows:

$$\left(1 - \frac{\Delta V}{V}\right)^{nV} = 1 - n\Delta V + \frac{nV(nV-1)}{2!}\frac{\Delta V^2}{V^2} - \frac{nV(nV-1)(nV-2)}{3!}\frac{\Delta V^3}{V^3} + \cdots$$

where n represents $\rho_0\left(\frac{r^T-1}{r-1}\right)$ or $\rho_0 r^T$. Because V is very large, nV in general is so large that nV-1, nV-2, . . . are practically equal to nV so that the binomial expansion may be written as

$$\left(1 - \frac{\Delta V}{V}\right)^{nV} \cong 1 - n\Delta V + \frac{n^2}{2}\Delta V^2 - \frac{n^3}{6}\Delta V^3 + \cdots \tag{13}$$

By substitution in equation (12) of series in the form of equation (13),

$$P(T,\Delta V,\rho_0,r) \cong \rho_0 r^T \Delta V + \frac{{\rho_0}^2\left(r^T\right)^2}{2}\Delta V^2 - {\rho_0}^2 r^T \left(\frac{r^T-1}{r-1}\right)\Delta V^2 +$$

$$\frac{{\rho_0}^3}{6}\left(\frac{r^T-1}{r-1}\right)^3 \Delta V^3 + \frac{{\rho_0}^3\left(r^T\right)^2}{2}\left(\frac{r^T-1}{r-1}\right)\Delta V^3 + \frac{{\rho_0}^3 r^T}{2}\left(\frac{r^T-1}{r-1}\right)^2 \Delta V^3 \cdots \tag{14}$$

is obtained. When T is close to zero, r^T is small and only the first term of the series in equation (14) need be used. As T increases, the terms of higher order must be considered and r^T-1 becomes more nearly equal to r^T, because r is greater than 1. Equation (14) may therefore be rewritten as

$$P(T,\Delta V,\rho_0,r) \cong \rho_0 r^T \Delta V - \frac{\rho_0^2\left(r^T\right)^2}{2}\Delta V^2 - \frac{\rho_0^2\left(r^T\right)^2}{r-1}\Delta V^2 +$$

$$\frac{\rho_0^3}{6}\frac{\left(r^T\right)^3}{(r-1)^3}\Delta V^3 + \frac{\rho_0^3}{2}\frac{\left(r^T\right)^3}{r-1}\Delta V^3 + \frac{\rho_0^3}{2}\frac{\left(r^T\right)^3}{(r-1)^2}\Delta V^3 \ldots \qquad (15)$$

The first step in the derivation of equation (10) is the proof that P_M, the mode value of P corresponding to T_M for one set of values of the parameters ρ_0 and ΔV, is equal to P_M corresponding to another set of values. Two sets of values of ρ_0 and ΔV are indicated by adding the subscripts 1 and 2, and the corresponding variables are similarly indicated. With equation (3) in the form

$$T_M = \frac{\log(\log r) - \log \rho_0 \Delta V - \log 0.4343}{\log r} \qquad (16)$$

with values ΔV_1 and ΔV_2 of the parameter ΔV, with values $\rho_{0,1}$ and $\rho_{0,2}$ of the parameter ρ_0, and with r maintained constant, the equation

$$r^{T_{1,M}} \rho_{0,1} \Delta V_1 = r^{T_{2,M}} \rho_{0,2} \Delta V_2 \qquad (17)$$

is obtained by subtraction of the equation for $T_{2,M}$ from that for $T_{1,M}$. The mode probabilities by equation (15) are

$$P_{1,M} \cong r^{T_{1,M}} \rho_{0,1} \Delta V_1 - \frac{\left(r^{T_{1,M}}\right)^2}{2}\left(\rho_{0,1}\Delta V_1\right)^2 - \frac{\left(r^{T_{1,M}}\right)^2}{r-1}\left(\rho_{0,1}\Delta V_1\right)^2 \ldots$$

and

$$P_{2,M} \cong r^{T_{2,M}} \rho_{0,2}\,\Delta V_2 - \frac{\left(r^{T_{2,M}}\right)^2}{2}\left(\rho_{0,2}\,\Delta V_2\right)^2 - \frac{\left(r^{T_{2,M}}\right)^2}{r-1}\left(\rho_{0,2}\,\Delta V_2\right)^2 \ldots$$

Therefore, by equation (17), the separate terms in the series for $P_{1,M}$ and $P_{2,M}$ are equal and

$$P_{1,M} \cong P_{2,M}$$

Because for a given value of r the mode probability P_M is the same for all values of ρ_0 and ΔV, the probability function P ranges from zero to P_M for all values of ρ_0 and ΔV. To the value of the probability P_1 corresponding to the values $\rho_{0,1}$, ΔV_1, and T_1, there are values $\rho_{0,2}$, ΔV_2, and T_2 such that

$$P_1 = P_2$$

From equation (15) series expansions for P_1 and P_2 are obtained and substituted in this equation so that

$$r^{T_1} \rho_{0,1}\,\Delta V_1 - r^{T_2} \rho_{0,2}\,\Delta V_2 \cong \left[\frac{\left(r^{T_1}\right)^2}{2}\left(\rho_{0,1}\,\Delta V_1\right)^2 - \frac{\left(r^{T_2}\right)^2}{2}\left(\rho_{0,2}\,\Delta V_2\right)^2\right] + \left[\frac{\left(r^{T_1}\right)^2}{r-1}\left(\rho_{0,1}\,\Delta V_1\right)^2 - \frac{\left(r^{T_2}\right)^2}{r-1}\left(\rho_{0,2}\,\Delta V_2\right)^2\right] \ldots \quad (18)$$

For values of T close to zero, the probabilities P_1 and P_2 are given to a good approximation by the first term of the series in equation (15), and the right-hand member of equation (18) is therefore negligible. As T increases, the terms of second and higher order in equation (15) become appreciable, and the individual terms on the right-hand side of equation (18) are no longer negligible. But as T approaches T_M, the bracketed differences on the right-hand side of equation (18) approach zero according to equation (17). The differences on the right-hand side

of equation (18) are therefore negligible in the range of T from 0 to a value somewhat greater than T_M. Therefore, because P becomes negligible for T just a little greater than T_M (see fig. 3), the equation

$$r^{T_1}\rho_{0,1}\Delta V_1 \cong r^{T_2}\rho_{0,2}\Delta V_2 \tag{19}$$

is a good approximation in the range of T where P is of appreciable magnitude. If the log of equation (19) is taken, this equation may be rewritten as a transformation equation, which yields the displacement of a probability curve in the T coordinate as

$$T_2 = T_1 + \frac{\log (\rho_{0,1}\,\Delta V_1/\rho_{0,2}\,\Delta V_2)}{\log r} \tag{10}$$

Calculations of P for various values of ρ_0 and ΔV from equation (2) confirm the approximate validity of equation (10).

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TABLE I - COMPARISON OF MODES AND AVERAGES OF FREQUENCY-DISTRIBUTION CURVES

Diameter of hemispherical drops (microns)	Mode (°C)	Average (°C)	(Mode)-(average) (°C)
[1]Experimental values			
805	-16.6	-17.4	0.8
161	-23.3	-24.2	.9
69	-25.5	-25.2	-.3
34.5	-24.4	-26.2	1.8
8.75	-32.2	-32.1	-.1
Theoretical values			
1564	-15.8	-15.2	-0.6
156.4	-23.0	-22.6	-.4
72.6	-25.5	-24.9	-.6
33.70	-27.7	-27.3	-.4
7.26	-32.7	-32.1	-.6

[1]Data from reference 2.

TABLE II - VALUES OF ρ_0 AND CORRESPONDING WEIGHTS USED IN MAKING COMPOSITE CURVE

ρ_0 (cm^{-3})	Weight
1.0×10^{-3}	2
2.64×10^{-4}	4
1.05×10^{-4}	2
5.7×10^{-5}	2
3.7×10^{-5}	2
2.6×10^{-5}	1

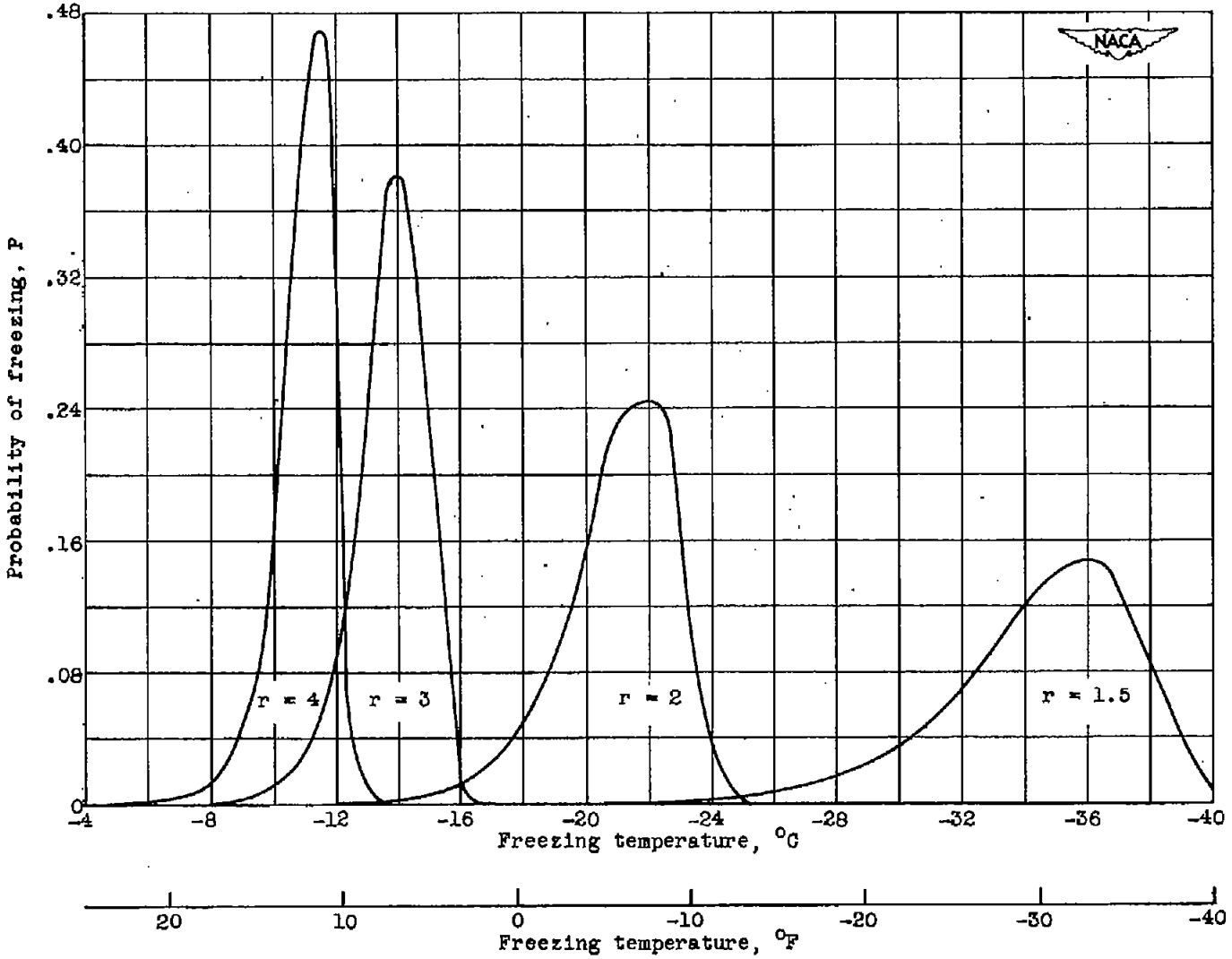


Figure 1. - Probability curves for various values of r computed from exact equation with $1-\Delta V/V = (\mu-1)/\mu = 1 - 10^{-8}$, $\Delta V = 10^{-3}$, $V = 10^{5}$, and $\rho_0 = 2.0 \times 10^{-4}$.

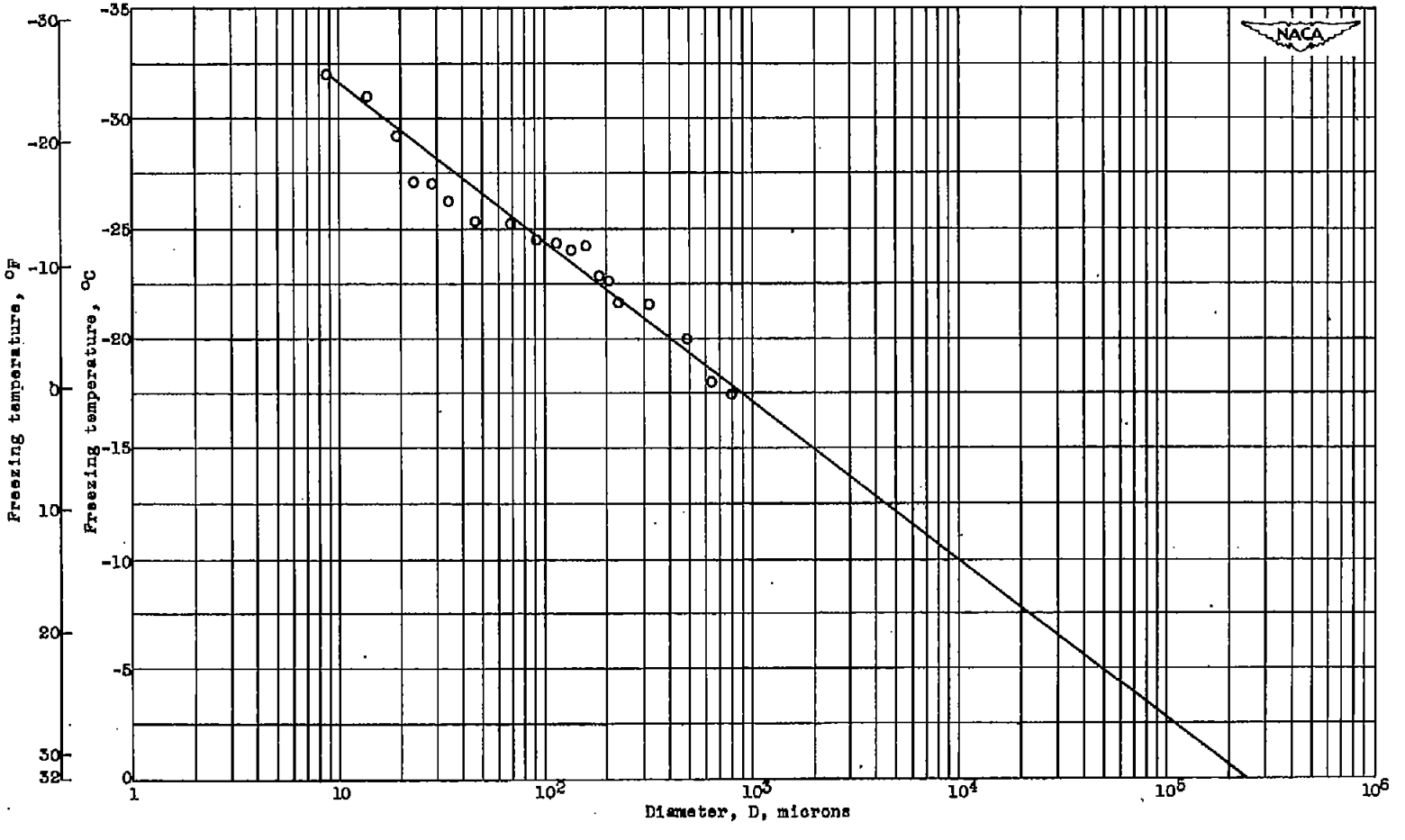
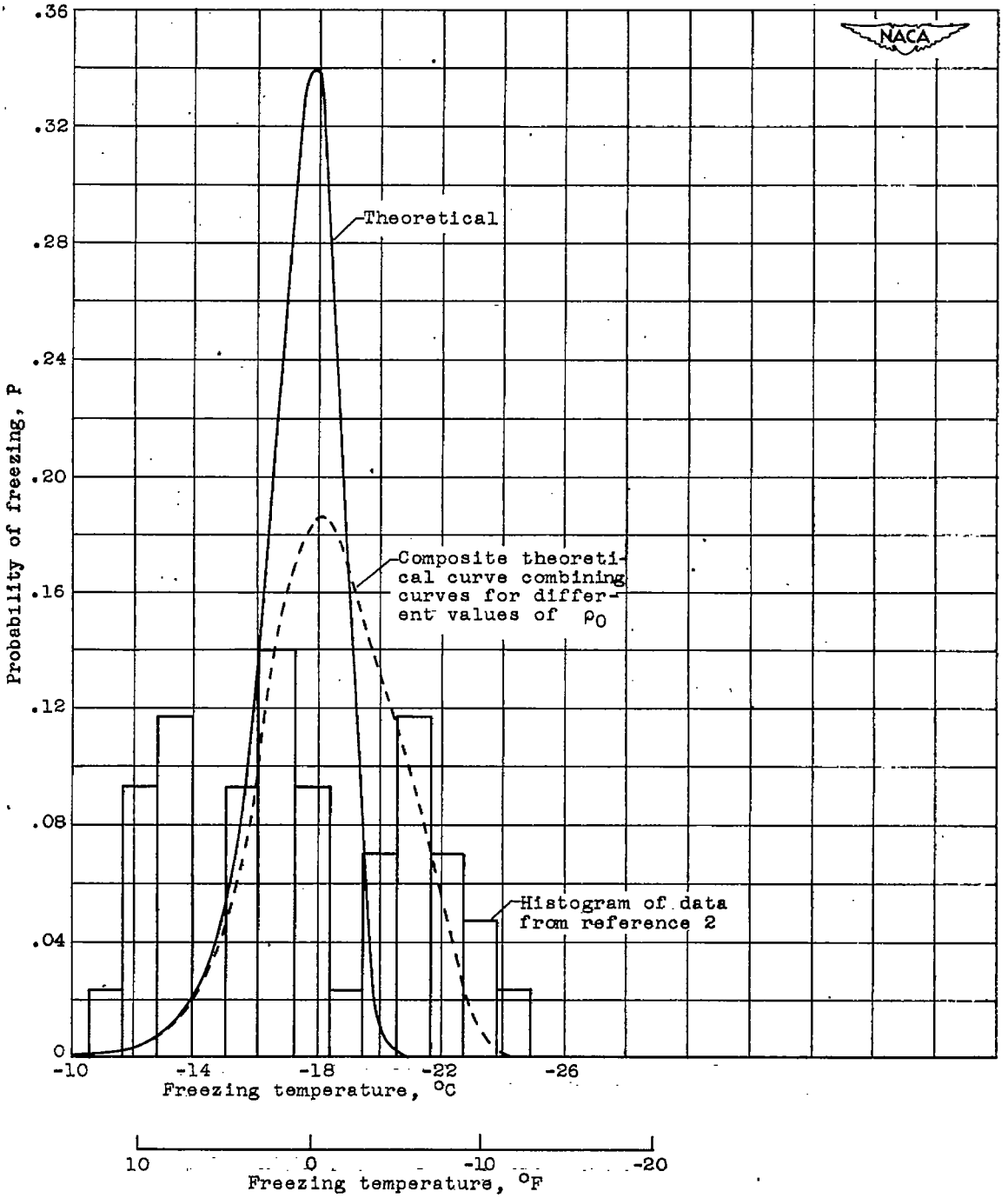
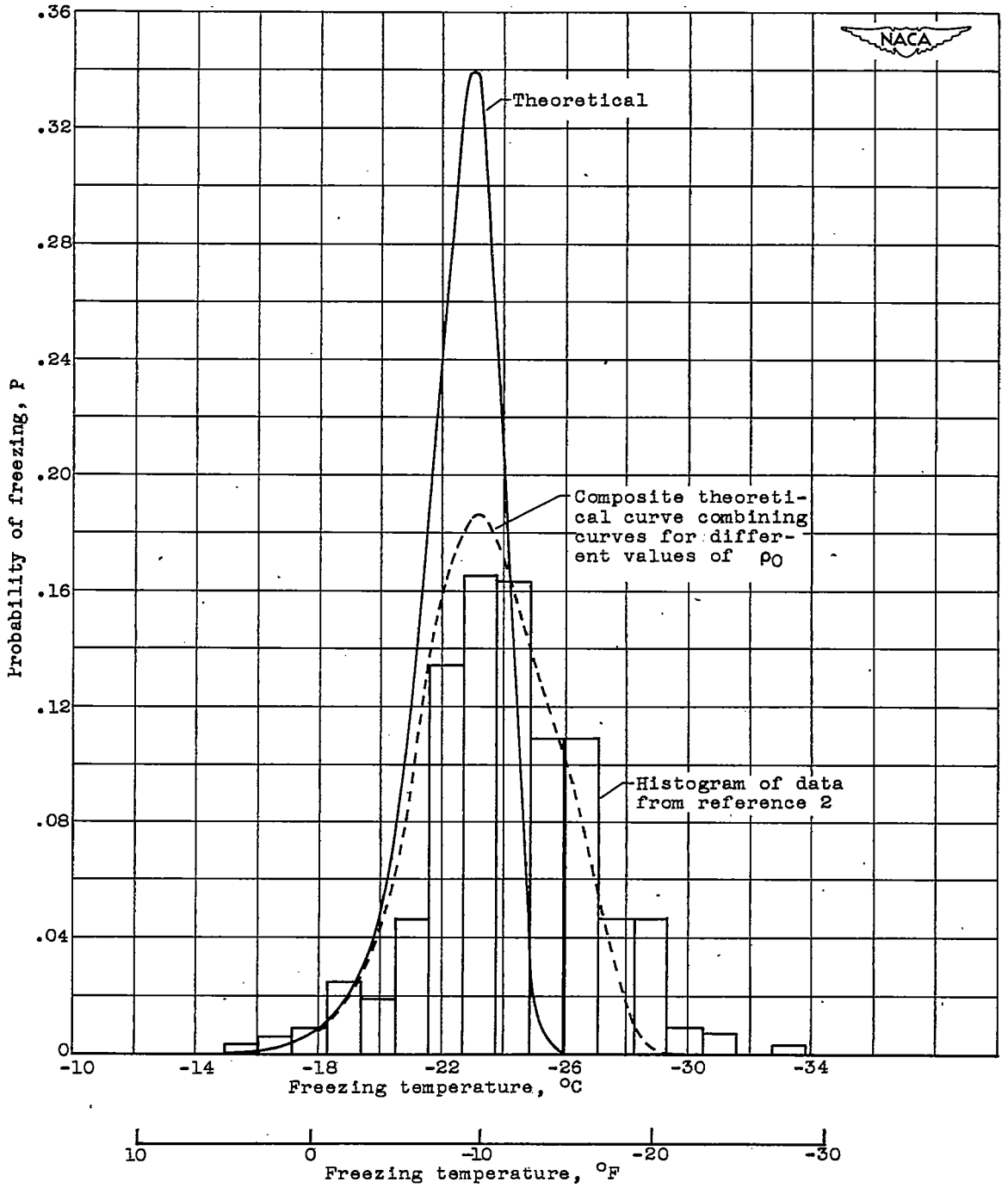


Figure 2. - Straight line fitted to data from reference 2 for diameter D against average freezing temperature.



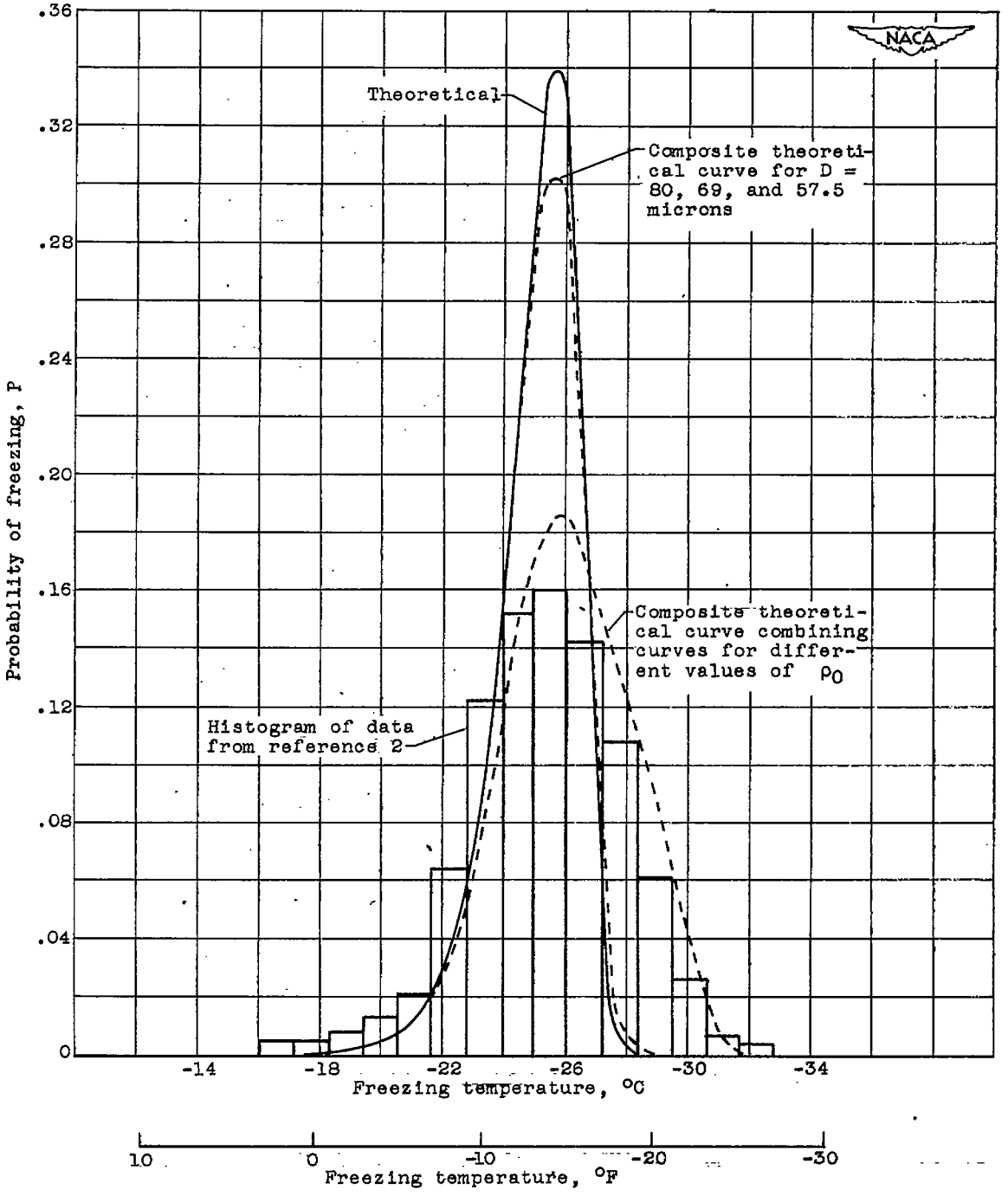
(a) Diameter, D, 805 microns.

Figure 3. - Comparison of theoretical and experimental probability curves.



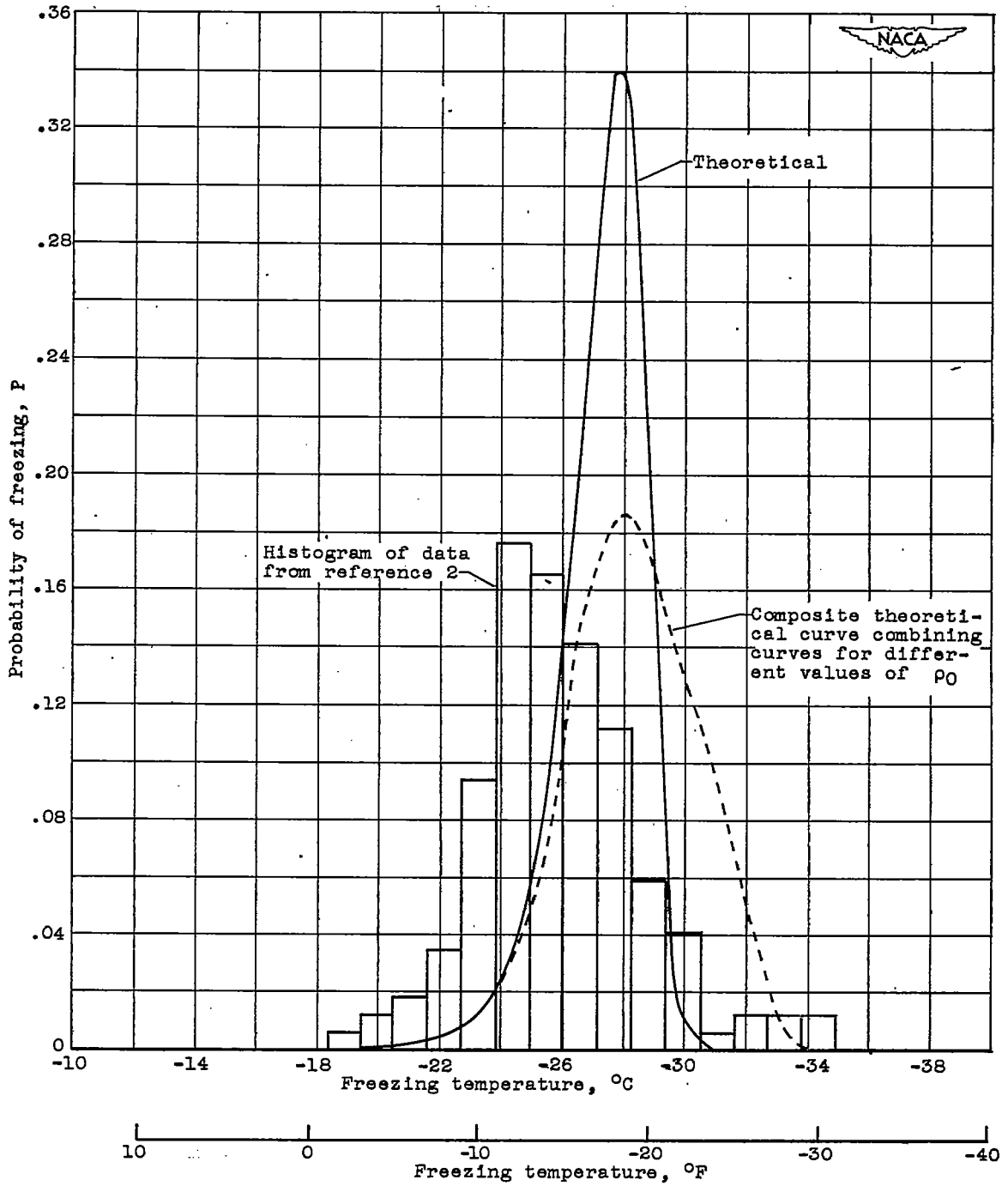
(b) Diameter, D, 161 microns.

Figure 3. - Continued. Comparison of theoretical and experimental probability curves.



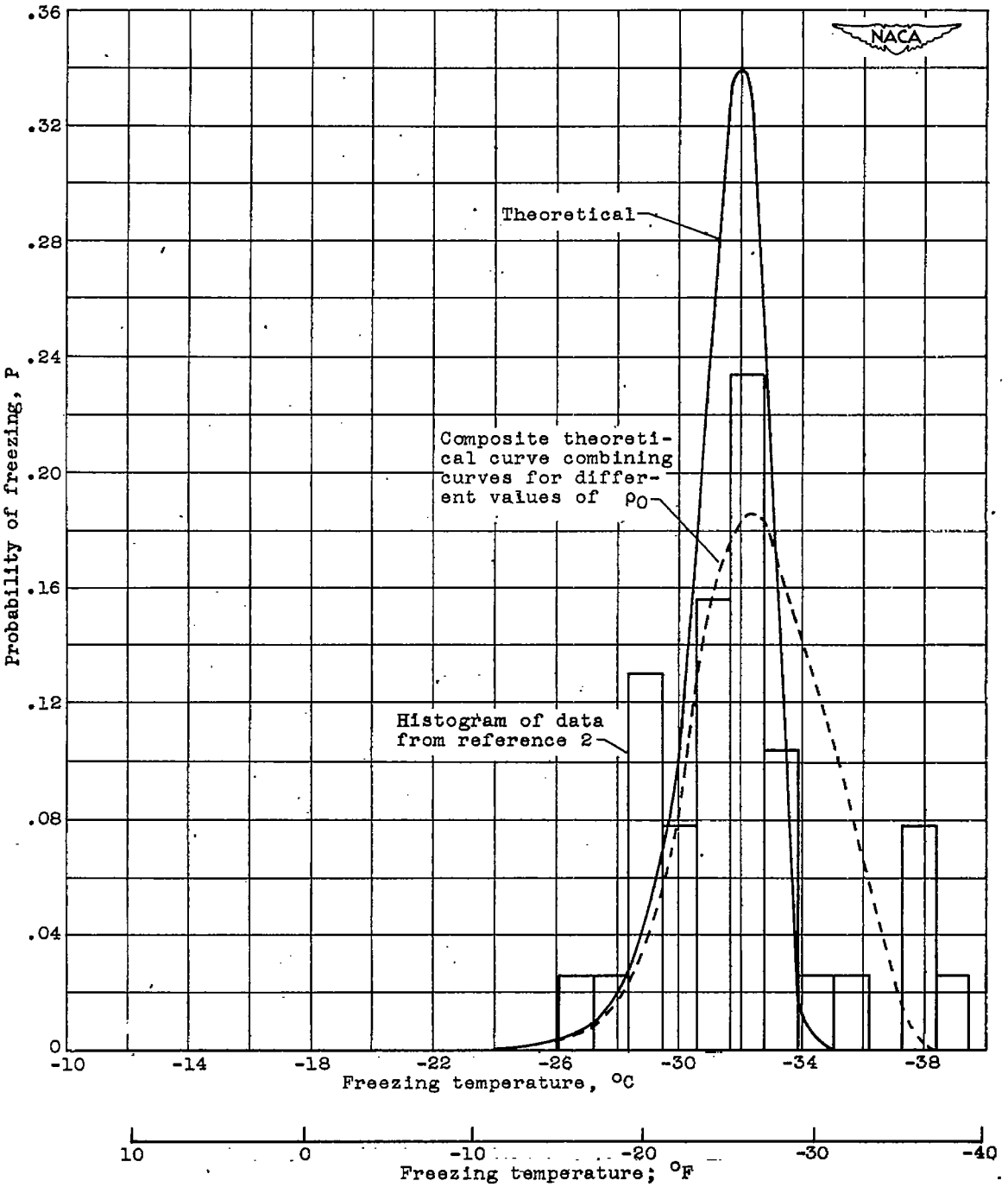
(c) Diameter, D, 69 microns.

Figure 3. - Continued. Comparison of theoretical and experimental probability curves.



(d) Diameter, D, 34.5 microns

Figure 3. - Continued. Comparison of theoretical and experimental probability curves.



(e) Diameter, D, 8.75 microns.

Figure 3. - Concluded. Comparison of theoretical and experimental probability curves.

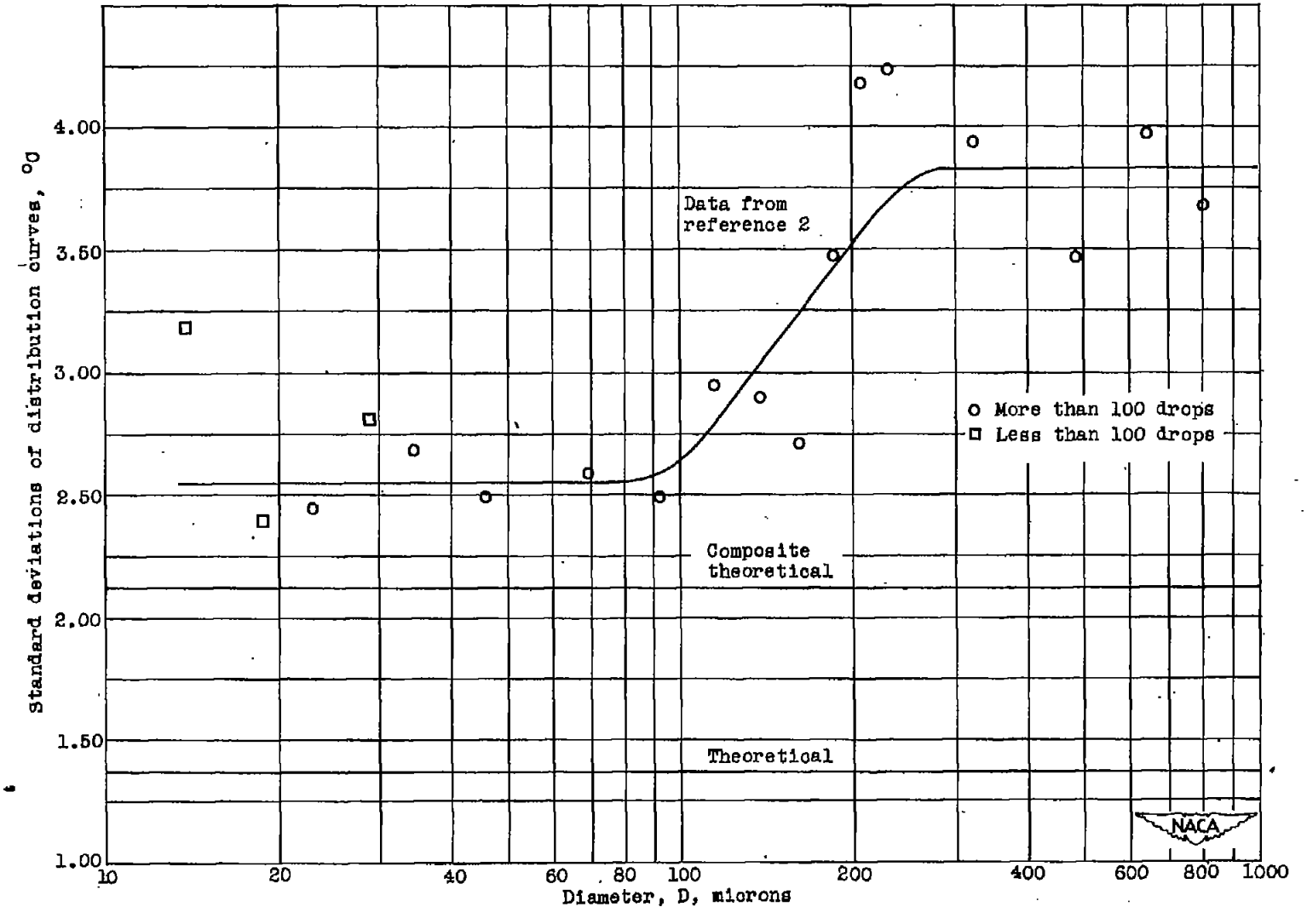


Figure 4. - Comparison of standard deviations of theoretical distribution curves with those of experimental curves.